

NEW APPROACHES TO PHASE EQUILIBRIUM MEASUREMENTS IN CONTINUOUS FLOW SYSTEMS AT HIGH PRESSURES AND TEMPERATURES.

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INTRODUCTION

Recently, the development of continuous flow supercritical processes has increased and research in this field is carried out in many universities all over the world. Processes under supercritical conditions are complex problem and the outcome of supercritical reactions can depend on the phase state of the reaction mixture [1]. Thus it is important to establish the phase behaviour inside the flow reactor.

In the frames of Green chemistry, many chemical reactions and processes e.g. extraction or impregnation involve high compressed gases or supercritical fluids (SCFs) as a solvent [1, 2]. Such solvents provide opportunities which can not be reached using conventional solvents; furthermore they are environmentally safe. The most commonly used fluids are CO₂ and H₂O; both of them have interesting and unique properties under supercritical conditions. For CO₂, at T = 31.1°C, P = 73.8 bar and, for H₂O, T = 374.2°C, P = 220.5 bar [3]. Most operations with SCFs are carried out in special stainless steel reactors, using stainless steel capillary to connect all the parts of equipment. Such systems do not permit researchers to observe what is happening inside the reactor. Information about phase behaviour can be crucial: conversion and composition of the products depends on it as shown by recent work from Nottingham [4]. There are many methods for measuring phase equilibria at high pressures and they have been exhaustively reviewed and classified by Christov and Dohrn [5]. Our research group is particularly interested in dynamic synthetic methods to locate phase transitions for the following reasons. Dynamic methods mimic conditions in continuous flow reactors; this means that starting materials are pumped continuously through a reactor with a fixed catalyst bed and the products are also collected continuously. Synthetic methods are suited to chemistry because, when doing reactions, we deal with given compositions and require phase envelopes for those particular components at set concentration.

THE “HOLEY” FIBRE METHOD

Holey fibres (silica capillaries with a numbers of channels running through them) are used for continuous sampling of a fluid. Such sampling does not disturb the equilibrium even in a relatively small measuring chamber. The fibre can be incorporated into a continuous flow system. In our case, a standard continuous flow apparatus was used, but the catalyst bed and reactor were replaced by a measuring chamber. The flow of mixture passed through the chamber and onto the tip of the fibre which points upstream. A small proportion of the flow goes down the fibre while the majority continues through the system to the back pressure regulator.

Samples of the mixture flowing down the holey fibre are then analysed by a flame ionisation detector (FID) salvaged from a gas chromatograph. The FID only responds if a flammable compound passes through it. In our case, nonflammable solvents such as water or CO₂ do not

give any signal. The second component of the mixture is organic, like acetone and ethanol, and gives a good signal on the FID. The intensity of the signal depends on the amount of flammable material passing through the FID. Therefore, if the fluid is in the vapour phase, the FID gives a low signal. But, if the system is in the liquid phase – a strong high signal. In the two phase region a noisy signal is expected as slugs of liquid and vapour reach the FID.

RESULTS AND DISCUSSION

The holey fibre method was tested on two well known systems, water + ethanol and CO₂ + acetone. Phase diagrams of the systems are presented in Figure 1a and 1b respectively. Results obtained by the holey fibre method are in good agreement with literature data. Detailed information on the holey fibre method and phase equilibria studies can be found in our recently published paper [6].

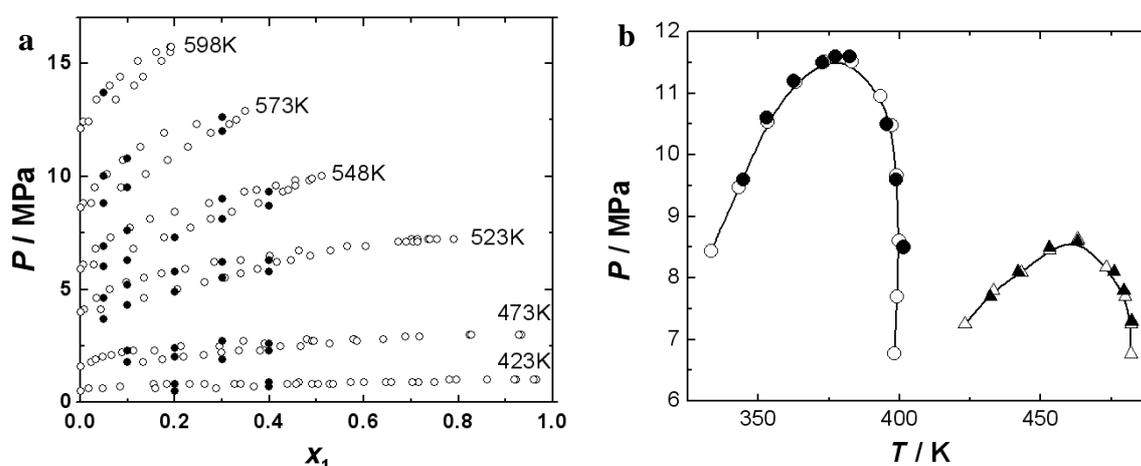


Figure 1a – P/T phase diagram for the acetone(x₁) + CO₂(x₂) system. This work. (●): x₁ = 0.2, (▲): x₁ = 0.7; Wu et al. [7] (○): x₁ = 0.2, (△): x₁ = 0.7. **1b** – P/X phase diagram for binary mixture ethanol (x₁) + H₂O (x₂). (●): this work; (○): Barr-David and Dodge [8]. Pictures reproduced from [6] © American Chemical Society.

THE GOLDEN GATE ATR METHOD

The Specac Golden Gate (GG) Attenuated Total Reflectance (ATR) cell is an accessory for IR spectrometers which gives possibility to perform ATR analysis of either liquids or solids; at atmospheric pressures or at high pressures and temperature. A schematic diagram of the GG equipment is showed below in Figure 2a. In this work the GG ATR cell is used to detect phase changes in single and binary mixtures.

The intensity of the peaks in the ATR spectra depends on the absorption of light by the fluid in immediate contact with the ATR crystal. The “working layer” of the fluid is about 0,5 – 5 μ depending on the spectrum region. Therefore if there is a vapour phase in the GG cell, the absorption of the light is low and the intensity is low. When the system crossed into the liquid phase, absorption is much higher and the peak intensities rise dramatically, because the liquid is much denser than the vapour. Then, it is possible to change either temperature or pressure and to collect spectra every 5-10 minutes until further significant changes in peak heights are detected.

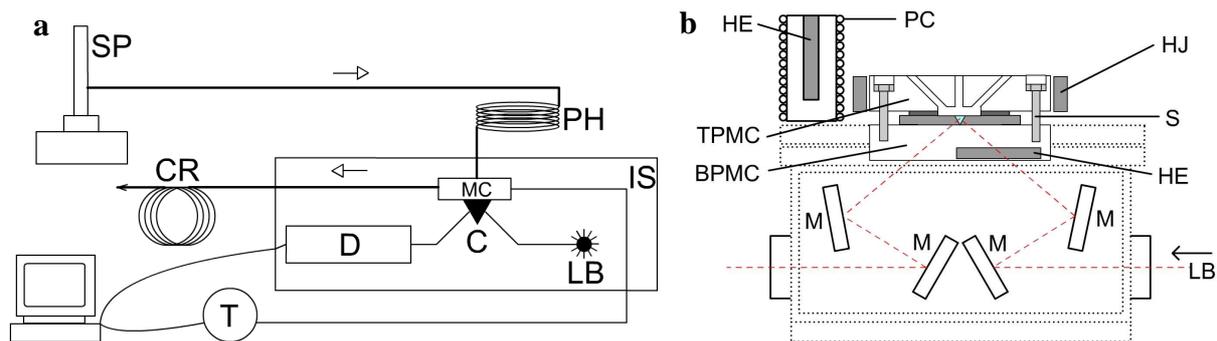


Figure 2a – Scheme of The GG equipment. SP - syringe pump; PH - preheater; IS-IR spectrometer; MC - measuring chamber; CR - capillary restrictor; LB - light beam; C - crystal of the golden gate; D - detector; T - temperature logger. **2b** – Scheme of the Golden Gate (GG) High Pressure ATR cell. Part A – before modification, part B – after. TPMC - top part of measuring chamber; BPMC - bottom part of measuring chamber; S - tightening screws; HE - heating element; M - mirrors; LB - light beam; PC - preheater; HJ - heating jacket;

Golden gate cell was connected to a supercritical system which consists of syringe pump (ISCO pump D series), preheater coil (5m of 1/16 inch stainless steel tube), the GG itself acts as the measuring chamber, and a capillary restrictor (1/16 inch PEEK tube, 3m long with inner diameter 127 μm). Temperature is controlled by thermocouples at the top and the bottom of the chamber and third for the preheater. Extra thermocouples were placed in the measuring chamber and in the “jacket” of the heating block at the top of measuring chamber to log the temperature during measurements. Pressure was controlled by the syringe pump and monitored by an extra pressure transducer placed just downstream of the measuring chamber. Several modifications were made to allow the GG to work with SCFs at high temperature and pressure. A new top plate of the cell was designed and constructed in the workshops of Nottingham University. It has three ports for standard 1/16 inch HIP fittings, so that the pipework can be disconnected in the event of blockages. An enlarged picture of the measuring chamber is shown in Figure 2b. To increase maximum operating pressure a groove was machined in the upper sealing surface of the measuring cell so that the gasket can be pressed into the groove when the cell is tightened. Temperature stability was improved by adding extra heating element to the top part of the GG.

RESULTS AND DISCUSSION

Three single component systems have been measured so far, water, ethanol and methanol. As shown in figure 3a there was good agreement with literature data for the vapour curves in all three cases. Typical experiment for these single fluids was done as follows. At the start background spectrum was recorded at low pressure and at set temperature, and then the pressure was ramped up to higher values. Absorbance at low pressure is very low; therefore, before the system switches to liquid phase, all spectra are similar and close to zero. When system is in liquid phase, the absorbance is much higher and peaks grow dramatically indicating the phase change.

Water + ethanol system was chosen to validate the GG ATR method for two component systems. Such system had been widely investigated in our group earlier using different technique. It was decided to cover one envelope for water ethanol system at temperature 250°C. The pattern of growth of the peaks is rather different from to single component systems.

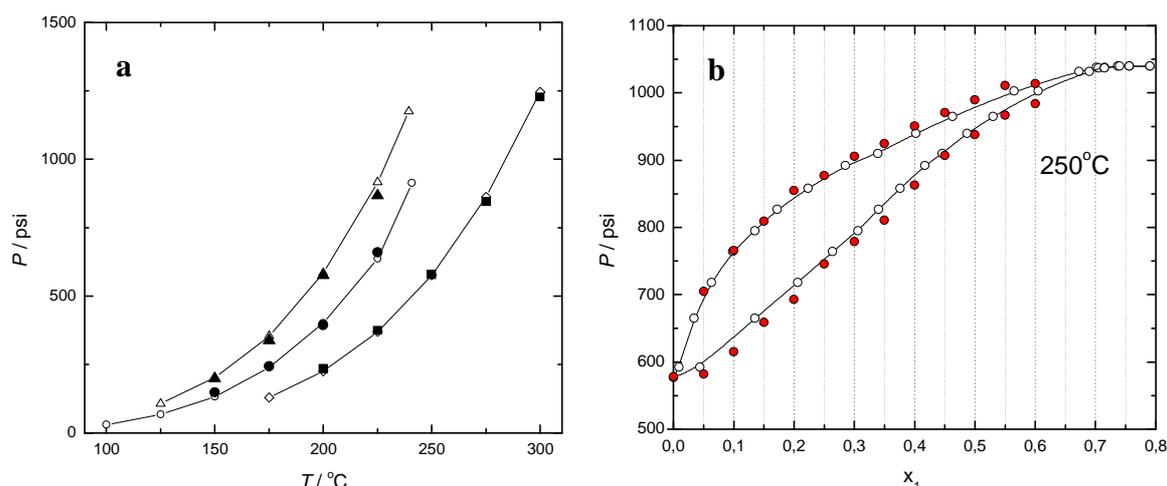


Figure 3a - P/T diagram for three single component systems is presented. ○ - literature data for Ethanol System; ● - experimental data for Ethanol System; □ - literature data for Water System; ■ - experimental data for Water System; △ literature data for Methanol System; ▲ literature data for Methanol System. Literature data is taken from Nist Webbook. **3b** - P/x diagram for two component system Water – Ethanol at temperature 250°C. ○ - literature data [8]; ● - experimental data.

At the beginning of the experiment the peak growth is the same as for single component mixtures, but beyond the dew point peaks continue to change their heights instead of stopping growing. Peaks of water go down, while peaks of ethanol go up. And then, at a certain point, the peaks stop changing their relative heights. This is the bubble point. Such behaviour occurs because the composition of liquid phase in the two phase region is changing as the pressure is tuned. But, after the system switches from the two phase region to a single liquid phase, the composition is fixed.

CONCLUSIONS

Two new dynamic synthetic methods have been developed to perform phase equilibria measurements at high pressures and temperatures. The holey fibre method is based on detecting the change in FID signal of a sample taken via a hollow capillary fibre. The Golden Gate ATR method is based on the change in IR absorbance of a mixture when it changes phase state. Both methods have been validated on well known systems. With the holey fibre, water + ethanol and CO₂ + acetone systems have been investigated. The Golden Gate ATR method has been tested on three single component systems, such as: water, ethanol and methanol; and on the two component mixture – water + ethanol. Good agreement between our experiments and literature data were found.

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